

## IMPROVEMENTS IN CONTACT RESISTIVITY AND THERMAL STABILITY OF Au-CONTACTED InP SOLAR CELLS

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Specific contact resistivities for as-fabricated Au contacts on n/p InP solar cells are typically in the  $10^{-3} \Omega\text{-cm}^2$  range, but contact resistivities in the  $10^{-6} \Omega\text{-cm}^2$  range can be obtained if the cells are heat treated at 400°C for a few minutes. This heat treatment, however, results in a dramatic drop in the open circuit voltage of the cell due to excessive dissolution of the emitter into the metallization. We have found that low values of contact resistivity can be secured without the accompanying drop in the open circuit voltage by adding Ga and In in the Au metallization. We will show that Au contacts containing as little as 1% atomic Ga can suppress the reaction that takes place at the metal-InP interface during heat treatment, while exhibiting contact resistivity values in the low  $10^{-5} \Omega\text{-cm}^2$  range. Similarly, we have found that the deposition of the alloy  $\text{Au}_9\text{In}_4$  on InP can inhibit all the metallurgical reactions which take place at the metal-InP interface even when heat treated at 400°C for many hours. We will present detailed explanations for the observed superior thermal stability of these contacts when compared to Au-only contacts. In addition, we will show that the very low contact resistivities observed with Au on n-InP when heat treated at 400°C is due the formation of the compound  $\text{Au}_2\text{P}_3$  at the metal-InP interface.

### INTRODUCTION

Ohmic contacts to III-V solar cells have not traditionally met all of the requirements expected of them. Ideally, these contacts should show negligibly low contact resistance, react minimally with the semiconductor substrate yet remain adherent, and be stable with aging at operating temperatures. These requirements are more stringent for the front emitter contacts than for the back base metallization.

For the front emitter contacts of III-V cells to have a negligible contribution to the series resistance, the contact resistivity  $\rho_c$ , should be in the low  $10^{-3} \Omega\text{-cm}^2$  range for one sun and in the low  $10^{-5} \Omega\text{-cm}^2$  range for 100X operations (ref. 1,2,3).  $\rho_c$  values two orders of magnitude higher than those for the front contacts are normally adequate for the back base contacts (ref. 2). Post-fabrication high temperature contact heat treatment or prefabrication semiconductor surface ion damage methods are normally used to obtain low resistance ohmic contacts (ref. 4 to 7). Both of these techniques, however, can be destructive for devices with shallow emitters such as n/p InP homojunction solar cells.

Ideally, a contact system should exhibit low contact resistance as-fabricated and also should be able to withstand thermal stress, such as high operating temperatures or radiation damage annealing, without compromising emitter integrity. Traditionally used Au and Au-based contact systems can not adequately satisfy either of the above criteria. However, we have found that the addition of small amounts of Ga or In to Au contacts not only lowers the as-fabricated  $\rho_c$  by an order of magnitude compared to Au-only contacts, but it also suppresses the metal-InP solid state interactions that normally occur at elevated temperatures. Our investigation of the Au-InP system and the mechanisms involved in contact formation (ref. 8 to 11), have enabled us to explain the superior thermal stability of these contacts as compared to Au-only contacts.

We will present the results of our study on Au-Ga and Au-In contact systems to n-InP and will also

provide an explanation for the observed two-to-three order of magnitude drop in contact resistivity of Au on n-InP at 400°C.

## EXPERIMENTAL

Epitaxially grown n/p InP diodes used in our study were obtained from the Spire Corporation. n-type emitters were 0.2  $\mu\text{m}$  thick with a doping density of  $1.7 \times 10^{18} \text{ cm}^{-3}$  (Si). The p-type (100) substrates were Zn doped to about  $8 \times 10^{16} \text{ cm}^{-3}$ . The Transmission Line Method (TLM) (ref. 12) was used to measure specific contact resistivity of the contacts on n/p diodes, and the Cox & Strack (C&S) method (ref. 13) was used to measure contact resistivity of the contacts made to bulk n-InP (100) substrates doped to about  $5 \times 10^{18} \text{ cm}^{-3}$  (S).

Contact deposition was by e-beam evaporation at a pressure in the  $10^{-6}$  Torr range. Au-Ga contacts were made by sandwiching 20Å (1% atomic) and 200Å (9% atomic) Ga layers between two 900Å layers of Au. The Au-In deposition technique has been described elsewhere (ref. 9). The metallization thickness for all Au and Au-In contacts was 2000Å. Also contacts referred to as as-fabricated have undergone mild heat treatments (110°C, 30 min.) during photolithographic processing. Also, The diodes were contacted on the base with ohmic Au-Zn metallization.

In order to monitor the degree of emitter dissolution/perforation caused by the heat treatment process, we observed the n/p diode current-voltage (I-V) characteristics. As a measure of I-V quality, we arbitrarily defined a diode conduction voltage  $V_1$ , as the voltage at which the forward current through the TLM patterned diode with an area of  $5.6 \times 10^{-3}$  was 1 mA. A good n/p junction should exhibit a  $V_1$  of about 900 mV. Lower values of  $V_1$  indicate a degraded emitter.

All heat treatments were performed in a rapid thermal annealing (RTA) furnace in a forming gas ambient. The compositional depth profile analysis of the contacts was performed via x-ray photoelectron spectroscopy (XPS), that was specifically calibrated for use with the Au-In binary system (ref. 14).

## RESULTS

### I. Au-Ga CONTACTS

The motivation to add Ga to Au was provided by the phosphorus release studies of Mojzes *et al.* (ref. 15), where it was shown that adding Ga to Au contacts on InP was effective in suppressing the release of P during heat treatment. We know from our previous studies of the Au-InP system (ref. 8 to 10) that the interaction of Au with InP is always initiated by the dissolution of In into Au followed by the release of P. Therefore, suppressing the release of P through Ga addition to Au was an indication that the dissolution of In was also suppressed. Fig. 1 shows XPS depth profiles of Au-only and Au-1%Ga contacts on InP heat treated simultaneously at 355°C for 40 minutes. As shown, addition of only 1% Ga to Au can suppress the metal-InP interaction significantly.

Fig. 1 also shows that Ga addition to Au eliminates the characteristic In peak at the free surface of the metal observed in Au-InP couples even at room temperature (ref. 11, 16, 17), replacing it with a Ga peak. The absence of this In peak indicates that Ga is somehow preventing In from diffusing dissociatively, i.e. interstitially, in the Au lattice (ref. 8). The presence of a Ga peak, on the other hand indicates that Ga is itself being transported dissociatively in Au. Therefore, it is apparent that Ga, by saturating the interstitial sites in Au prevents In from entering the interstitial pool, thus suppressing the metal-InP interaction. In fact, the presence of Ga in Au suppresses all the solid state phase transitions in the Au-InP system (three stages) which involve the formation and diffusion of the In interstitial (ref. 18).

Fig. 2 illustrates the effectiveness of adding 9%Ga to Au in preserving the emitter integrity of a n/p

diode during heat treatment. As shown, the diode with Au-only metallization begins to fail at about 370°C, whereas minimal degradation is observed for the Au-9%Ga contacted diode up to 440°C. It should be noted that addition of 9% Ga to Au is more effective in suppressing the metal-InP interaction than is the addition of 1% Ga to Au. This is due to the fact that some Ga interstitials take substitutional positions in the Au lattice during heat treatment, thereby losing their ability to prevent In interstitials to enter the lattice. However, if sufficient amount of Ga is added to Au (i.e., 9%) so that some Ga atoms can remain in their interstitial positions during heat treatment, the In interstitial entry into the Au lattice can still be prevented.

In addition to the desirable reaction suppressing effects of Ga addition to Au, we have found that Ga addition improves the contact resistance of Au contacts. As shown in Fig. 3, Au-9%Ga contact shows a one to two order of magnitude lower contact resistivity than the Au-only contact up to 400°C. A minimum  $\rho_c$  value of  $3.2 \times 10^{-5} \Omega\text{-cm}^2$  is observed with Au-9%Ga contacts at the 270-280°C range. The contact resistivity values of Au-1%Ga contacts are very similar to those of Au-9%Ga contacts.

Since Ga causes the In entry rate into Au to slow down, P atoms released at the metal-InP interface have time to dissipate. It has been shown that a decrease in the amount of accumulated P at the metal-InP interface can result in lower contact resistivity values (ref.18). This may explain the lower  $\rho_c$  values observed with Au-Ga contacts as compared to Au-only contacts.

## II. Au-In CONTACTS

Another method to inhibit In entry into the Au lattice, and thus improve  $\rho_c$ , is to introduce In into the metallization in place of Ga. But since the addition of In to Au in amounts less than 10% atomic (the saturated solid solution of In in Au) can not suppress the metal-InP interactions, we deposited Au-In mixtures ranging from 12 to 35% In. Fig. 4 shows the effect of adding In (and Ga) to Au for as-fabricated contacts on n-InP. As shown, Au-In and Au-Ga as-fabricated contacts have about an order of magnitude lower contact resistivity than Au-only contacts.

To examine the thermal stability of Au-In contacts at elevated temperatures, we subjected Au contacts containing 23, 35, and 30% ( $\text{Au}_9\text{In}_4$ ) In to isothermal annealing at 400°C. The compound  $\text{Au}_9\text{In}_4$  was specifically chosen because it is the end product of the third stage of a series of solid state interactions in the Au-InP system (ref. 10), and therefore, was expected to withstand thermal stress at elevated temperatures. Indeed, as shown in Fig. 5, n/p diodes contacted with  $\text{Au}_9\text{In}_4$  showed no degradation at 400°C for at least 12 hours. Also evident from the figure is the fact that although the 23% and 35% In-Au contacts are not as stable as  $\text{Au}_9\text{In}_4$ , they are far superior than Au-only contacts.

In addition to their metallurgical stability, Au-In contacts show stable contact resistivities at 400°C. As shown in Fig. 6,  $\rho_c$  values in the low  $10^{-5}$  to low  $10^{-4} \Omega\text{-cm}^2$  range are obtainable with these contacts. Here again,  $\text{Au}_9\text{In}_4$  is more stable than other Au-In contacts.

## III. Au CONTACTS

Looking back, in Fig. 3, it is seen that although Au-only contacts show higher  $\rho_c$  values than the Au-Ga contacts at lower temperatures, at 400°C a two-to-three order of magnitude drop in contact resistivity is observed. We were able to correlate this resistivity drop with a phase transition (stage II) in the Au-InP system where the contact metallization is transformed to the pink colored compound  $\text{Au}_3\text{In}$  (ref. 9). This is illustrated in Fig. 7 where Au-contacted InP was heat treated at 353°C. As shown,  $\rho_c$  reaches a plateau in the low  $10^{-6} \Omega\text{-cm}^2$  range as the entire metal is converted to  $\text{Au}_3\text{In}$ .

The stage II phase transition, which is apparently responsible for this resistivity drop, is accompanied by three prominent physical changes in the Au-InP system. First is the conversion of the contact to the stable alloy  $\text{Au}_3\text{In}$ . Second, the compound  $\text{Au}_2\text{P}_3$  is formed at the metal-InP interface concurrent with the appearance of  $\text{Au}_3\text{In}$ , and finally the surface of InP beneath the contact becomes pitted (ref. 9).

In order to determine which of the above changes are responsible for the resistance drop, we designed the following experiment where various stage II products were selectively removed and replaced. To facilitate alignment and remasking of the contacts, we prepared five samples each having Au discs of various sizes on bulk n-type InP for contact resistivity measurement via the C&S technique. The contacts were heat treated at 390°C for 3 minutes to induce stage II phase transition. As shown in Fig. 8, all five samples exhibited ~two order of magnitude drop in  $\rho_c$  (note that here overall  $\rho_c$  values are lower than samples used for TLM measurements since the InP doping density is higher by ~factor of 3) (ref.19).

We then removed  $\text{Au}_3\text{In}$  and  $\text{Au}_2\text{P}_3$  from three samples (dark circles in Fig. 8), leaving a pitted InP surface, and only  $\text{Au}_3\text{In}$  from the remaining two samples (light circles) leaving  $\text{Au}_2\text{P}_3$  on the InP surface. As shown in the figure,  $\rho_c$  values for samples with  $\text{Au}_2\text{P}_3$  remained essentially the same after  $\text{Au}_3\text{In}$  removal. We then remasked all samples and redeposited a 2000Å layer of Au over original patterns. Again as seen in the figure,  $\rho_c$  values for samples with  $\text{Au}_2\text{P}_3$  did not change, but samples without  $\text{Au}_2\text{P}_3$  showed resistivity values nearly as high as their original as-fabricated values (note that pitted InP surface, having a larger area than the smooth surface, measures a lower  $\rho_c$  value than its true value).

From the above results, we can conclude that the observed large drop in contact resistance is due neither to the changes in the InP surface geometry nor to the presence of the  $\text{Au}_3\text{In}$  alloy, but in fact it is due to the formation of  $\text{Au}_2\text{P}_3$  at the metal-InP interface.

## SUMMARY

We have investigated Au-Ga and Au-In contact systems as front emitter metallization for use on n/p InP solar cells. Our major findings are as follows:

- 1). When Ga is added to Au, it precludes the entry of other species such as In and Au into the Au lattice.
- 2). Because In interstitial formation and migration are involved in all three stages of the Au-InP interaction, all aspects of the reaction of Au with InP are suppressed if sufficient interstitial Ga is present in the Au lattice.
- 3). The addition of as little as 1% atomic Ga into Au on n-InP reduces the as-fabricated contact resistivity by an order of magnitude.
- 4). Addition of various amounts of In to Au on n-InP can show as-fabricated contact resistivity values in the high  $10^{-5} \Omega\text{-cm}^2$  range.
- 5). The alloy  $\text{Au}_9\text{In}_4$  deposited on n-InP is metallurgically and electrically stable for many hours of heat treatment at 400°C.
- 6). The two-to-three order of magnitude drop in contact resistivity observed with Au on n-InP when heat treated at 400°C is the result of the formation of the compound  $\text{Au}_2\text{P}_3$  at the metal-semiconductor interface.
- 7). Finally, we have shown that Au-Ga and Au-In contact systems have lower contact resistivity and superior thermal stability than Au-only contacts to n-InP, and they are suitable candidates for use as the front emitter ohmic contacts to n/p InP solar cells for one sun or concentrator applications.

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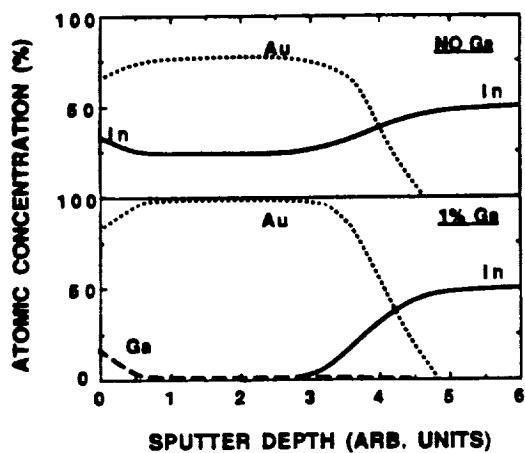


Fig. 1 XPS Compositional depth profiles for Au-only (upper) & Au-1%Ga (lower) contacts heat treated at 355°C for 40 minutes.

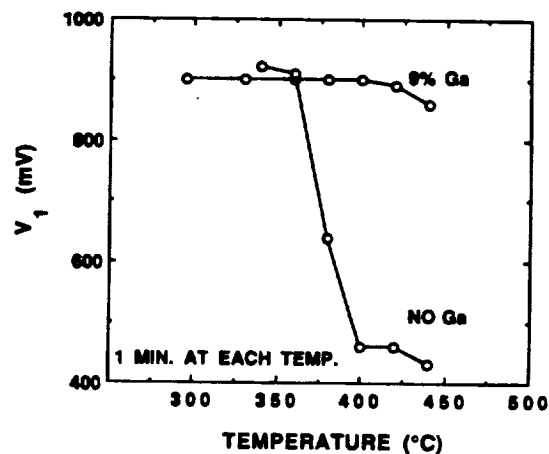


Fig. 2 The n/p diode conduction voltage Vs. temperature for Au-only & Au-9%Ga contacts.

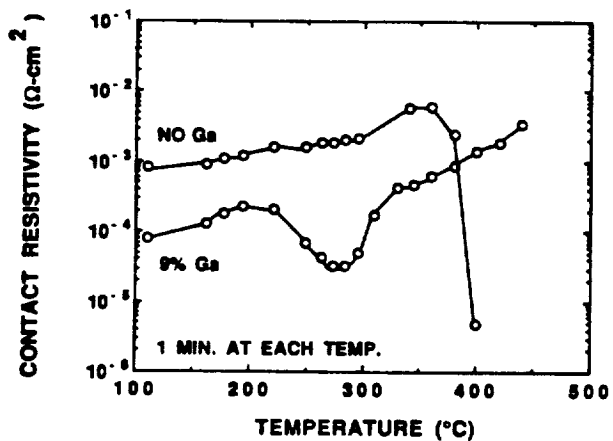


Fig. 3 The specific contact resistivity Vs. temperature for Au-only & Au-9%Ga contacts on n-InP.

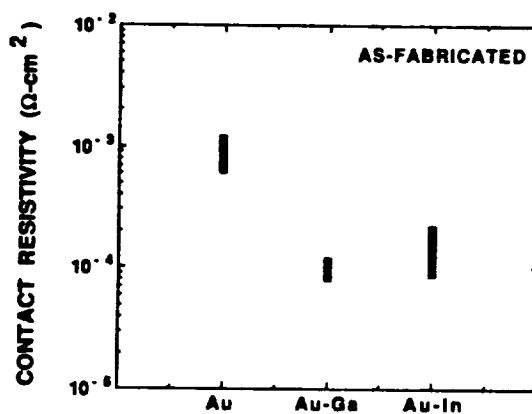


Fig. 4 As-fabricated contact resistivities for Au-only, Au-Ga, & Au-In contacts on n-InP.

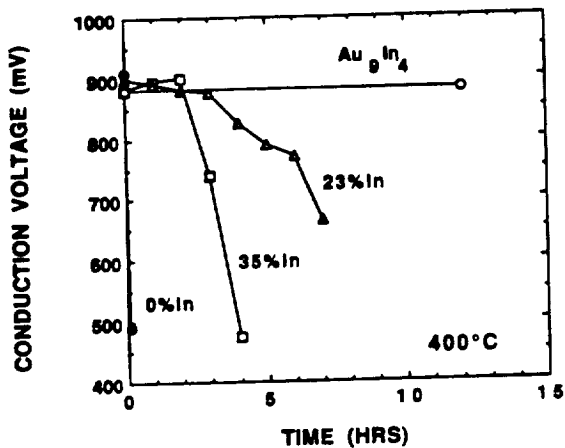


Fig. 5 The variation of the np diode conduction voltage with time for Au contacts containing various amounts of In at 400°C.

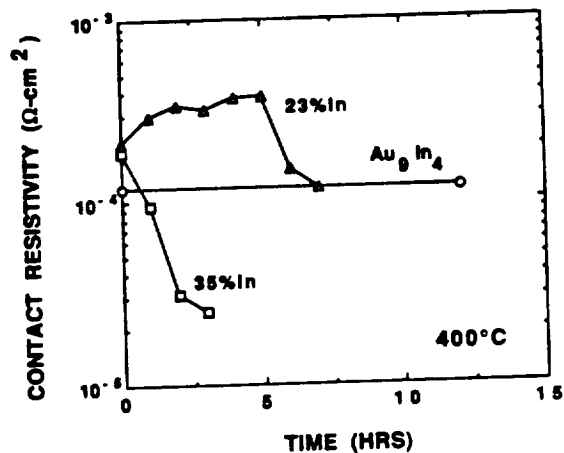


Fig. 6 The variation of contact resistivity with time for Au contacts containing various amounts of In at 400°C.

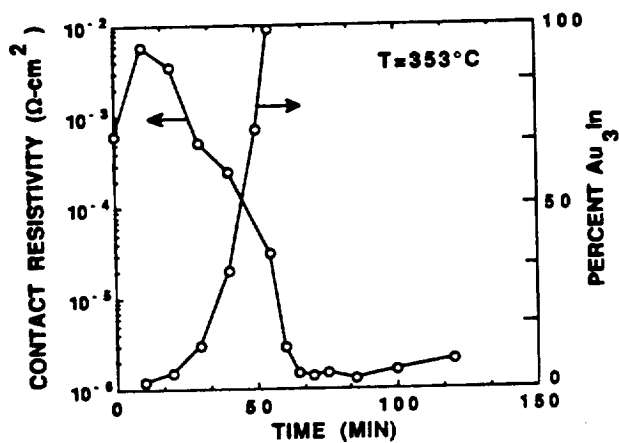


Fig. 7 Contact resistivity and percent Au(In)-to- $Au_3In$  conversion for Au-only contacts as a function of time at 353°C on n-InP.

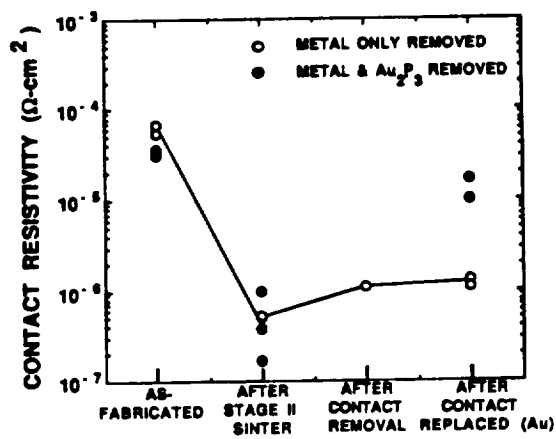


Fig. 8 The effect of contact removal & replacement on the specific contact resistivity.

